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To Mr. F.J. Kee
Director of Research

DETERMINATION OF TOTAL MERCURY IN WATER
INTERIM PROCEDURE

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The analysis of total mercury in water requires that stable organic mercury compounds be converted to inorganic mercury before analysis by continuous flow analysis with atomic absorption detection. A mixture of sulfuric acid, potassium dichromate and potassium peroxydisulfate was found to be most suitable for decomposition of organomercury compounds. However, reproducibility problems with both the digestion and analysis result in a detection limit of about 0.5 micrograms per litre, rather than the desired limit of 0.2 micrograms per litre.

1.0 INTRODUCTION

The determination of inorganic mercury in environmental water samples at sub-parts per billion level has been routinely accomplished in this laboratory and many others for several years using the cold vapour generation atomic absorption method. However, many environmental samples contain mercury in relatively stable organometallic form, and these are not detected by the simple cold vapour technique. This work reports on our studies of various digestion techniques intended to decompose the organomercury compounds into inorganic forms suitable for detection by the cold vapour technique.

Organomercury compounds can be present in environmental samples as a result of either biosynthesis, or from direct industrial pollution. It is estimated that as much as 60% of the mercury in a sample can be present in organic mercury compounds.

The cold vapour technique, which involves reduction of mercuric compounds to elemental mercury, sparging of the mercury from solution by a gas stream, and determination of the mercury by atomic absorption spectrometry, was also reviewed and enhanced in this

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study. In particular the choice of low-mercury reagents was considered, the continuous flow process for sample preparation and atomic absorption detection cell were reviewed and improved. The objective was to be able to measure total mercury in water at levels of 0.2 ppb, which is reportedly achievable by both the MOE laboratory and the CCIW laboratory.

2.0 COLD VAPOUR GENERATION METHOD

In atomic absorption analysis, the atomic species required for detection by the spectrometer are normally generated by thermal decomposition of molecular species in a flame or electrothermal atomizer. In the cold vapour technique volatile elemental mercury is carried to the spectrometer by a gas stream. The sample cell is only mildly warmed to prevent condensation of water vapour.

The inorganic mercury is reduced in two stages by the addition of hydroxylamine hydrochloride, followed by stannous chloride. Elemental mercury is then stripped from solution by an argon stream and passed into the light path of the atomic absorption spectrophotometer. The first reduction stage is used to eliminate excess oxidizing agents which would be present from the sample digestion stage which decomposes the stable organomercury compounds. The use of this preliminary reduction was found to produce more reliable results and better precision than occurred if a single stage process using an excess of stannous chloride was used.

The previously used cold vapour technique involved mercury vapour collection on silver foil as a preconcentration measure with subsequent evolution of mercury upon rapid heating of the foil. Frequent problems occurred, however, due to poisoning of the foil by other volatile species present in the samples. In addition, the method was extremely slow. Therefore, sample handling and preparation was automated using continuous flow analysis. The silver foil collection step was successfully eliminated with little loss in sensitivity because of the more compact design of the new set up. The polystyrene sample containers used in the autosampler were found to be suitable for this analysis even though the material is normally considered unsuitable because of potential contamination and the possibility of loss of cations by absorption. This probably resulted from the fact that the samples after digestion were very acidic.

3.0 DECOMPOSITION OF ORGANOMERCURY COMPOUNDS

Strongly oxidizing acidic conditions were expected to be most suitable for the decomposition of organomercury compounds. A variety of reagents and conditions were chosen, and evaluated on solutions containing methyl mercuric chloride, phenyl mercuric acetate, and diphenyl mercury. Methyl mercuric chloride is considered to occur most frequently in the environment, and is difficult to decompose.

The digestion procedures were tested with two concentrations (between 0.8 and 2.6 µg/L) of each organic compound and a set of inorganic standards and blanks. The sample size was 20 mL in each case. The results of the various digestion procedures investigated are summarized in Table 1.

TABLE 1

DIGESTION METHODS

Digestion Conditions	Mercury Blank (µg/L)	% Recovery (Average of 3 Samples)		
		Methyl Mercuric Chloride	Phenyl Mercuric Acetate	Diphenyl Mercury
1. Perchloric Acid (3 mL) 1 h @ 98°C	<0.1	69	93	128
2. Perchloric Acid (3 mL)(to fumes)	-	Random Scatter	Same	Same
3. Perchloric Acid (3 mL) + Sulfuric Acid (2 mL) (to fumes)	-	Random Scatter	Same	Same
4. Nitric Acid (3mL) + Sulfuric Acid (2 mL)(to fumes)	<0.1	42	0	0
5. Hydrogen Peroxide (30%;2mL) + Sulfuric Acid (3mL). Brought to boil.	0.3	4	75	78
6. Potassium persulfate (4% solution 1 mL) + sulfuric acid (3 mL) steam bath; 1 h	0.7	81	89	90
7. Potassium persulfate (4%; 1 mL) + potassium permanganate (2%; 1 mL) + sulfuric acid (3mL) Steam bath; 1 h	0.1	117	94	98
8. Potassium dichromate (2%; 1 mL) + potassium persulfate (4%; 1 mL) + sulfuric acid (3mL) Steam bath; 1 h	0.3	120	99	91

It was found that all methods which involve significant heating of the sample (above 100°C) resulted in high and variable losses of mercury. Best results were obtained with sulfuric acid, potassium persulfate, and either potassium permanganate or potassium dichromate.

Unfortunately, there was a large variation in the blanks which limited the precision of the analysis. Various combinations of aging plus filtration, oven drying, and ion exchange were used in attempts to purify the reagents. None of these procedures were successful.

Although potassium permanganate and potassium dichromate seemed to be equally efficient in decomposing organomercury compounds, it is recommended that potassium dichromate be chosen as the oxidizing agent since it is available in greater purity and is less likely to cause other interfering reactions.

4.0 PRECISION

The precision of the dichromate based method was evaluated at several concentrations using inorganic mercury standards as well as organic compounds. The results are summarized in Table 2.

Within-sample precision was evaluated by running the same sample repeatedly (3 times) on the cold vapour generation apparatus. Between-sample precision was obtained by putting 5 individual samples through the entire digestion-generation process. The range for each type of precision was found by repeating these studies on three different days.

The method suffers from poor precision at all stages. Until this situation can be improved, reliable data can be obtained only by doing all samples in triplicate. The detection limit also varies as a consequence of the variable performance, with an average value around 0.5 µg/L.

TABLE 2

PRECISION

Mercury Concentration (µg/L)	Within-Sample Precision (1 S.D.; N=3) (µg/L)	Between-Sample Precision (1 S.D.; N=5) (µg/L)
Blank	0.04 - 0.10	0.09 - 0.30
0.2	0.10	0.03 - 0.30
0.5	0.05 - 0.20	0.04 - 0.60
1.0	0.30 - 0.40	0.01 - 1.00
2.0	0.10 - 0.40	0.05 - 0.90
Methyl 0.9	0.10	0.05 - 0.30
Phenyl 1.3	0.10	0.03
Diphenyl 1.7	0.10 - 0.20	0.10 - 0.60

5.0 SUMMARY AND CONCLUSIONS

Digestion of aqueous samples with potassium dichromate, potassium persulfate and sulfuric acid was found to be the most reliable means of converting various organic forms of mercury to inorganic mercury which could then be determined by cold vapour generation and atomic absorption spectrophotometry. The method suffers from relatively poor precision necessitating the use of at least triplicate samples and resulting in a detection limit of about 0.5 µg/L mercury. Although adequate in many instances, a detection limit of 0.2 µg/L or better is considered desirable. The need for replicates results in high sample consumption and cost.

Further investigation is recommended in a number of areas:

1. The precision of the analysis can be improved by reducing the variability of the digestion stage. In-line digestion is recommended for evaluation. The precision of continuous flow methods is generally much better than that of manual procedures. In addition, losses of mercury during digestion would be reduced.

2. Blank levels can be reduced by using a combination of ultra-violet light irradiation and chemical digestion. The combined digestion method requires much less reagents, thereby decreasing the blanks. This would help to improve the detection limit.

3. The signal to noise ratio at low mercury concentrations can be increased by re-introducing a preconcentration step prior to the final measurement. Gold foil or gold precipitated on an inert matrix is recommended as the collection medium since it suffers from fewer interferences than silver. Although such a step would decrease the speed of the analysis, a significant increase in precision would allow the use of less replicates, thereby partially compensating for the slower analysis.

6.0 ACKNOWLEDGEMENT

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APPENDIX

ANALYTICAL PROCEDURE - DETERMINATION OF MERCURY IN WATER

1.1 Equipment and Supplies

1.1.1 Atomic absorption spectrophotometer (Varian Techtron AA4 or equivalent)

1.1.2 Mercury hollow cathode lamp

1.1.3 Cell. See Diagram 1

1.1.4 Variac voltage regulator

1.1.5 Strip chart recorder

1.1.6 Technicon Autoanalyzer sampler, manifold and pump

1.1.7 Argon cylinder, regulator, flow meter

1.1.8 Millipore filtration apparatus and 0.45 µm filters

1.1.9 Steam bath

1.1.10 Test tubes; 3 per sample and 1 per standard

1.2 Standardization

Run at least four standards covering the range 0.2 - 3.0 µg/L mercury at the beginning of every batch and one standard after every 10 samples.

1.3 Outline of Method

The samples are digested with sulfuric acid, potassium persulfate, and potassium dichromate. The treated sample is passed through a continuous flow analyzer system where it is reduced with stannous chloride. The mercury is swept from solution by an argon stream to a gas liquid separator. The gas stream is passed through a cell positioned in the light path of an atomic absorption spectrophotometer. The absorption of the mercury vapour is recorded.

1.4 Interferences

High levels of organic compounds interfere as well as gold (0.03), palladium (0.15), lead (0.01), tellurium (0.04), copper (100) and sulfide (20). Interference levels are in mg/L.

1.5 Concentration Range

The optimum concentration range in a solution is 0.5 to 3.0 µg/L mercury. The range may be extended upward by dilution.

1.6 Precision and Accuracy

Precision is typically 10-30% at 1 µg/L and recoveries at this concentration are generally quantitative within experimental limit.

1.7 References

1.7.1 Agemian, H. and Chan A.S.V., "Automated Method for the Determination of Total Dissolved Mercury in Fresh and Saline Waters by Ultraviolet Digestion and Cold Vapour Atomic Absorption Spectrophotometry", Analytical Chemistry, 1978, 50, 13-16.

1.7.2 El-Awady, A.A., Miller, R.B. and Easter, M.J., "Automated Method for the Determination of Total and Inorganic Mercury in Water and Wastewater Samples", Analytical Chemistry, 1976, 48, 110-116.

1.7.3 Goulden, P.D. and Afghan, B.K., "An Automated Method of Determining Mercury in Water", Advances in Automated Analysis, 1973, p 317.

1.8 Reagents and Solutions

1.8.1	4% Potassium Persulfate	Dissolve 40 g of "suitable for Hg determination" grade potassium persulfate in 800 mL of deionized water. Make up to 1 L using a volumetric flask and filter through an 0.45 µm filter. Make up fresh weekly.
1.8.2	2% Potassium Dichromate	Dissolve 20 g of "suitable for Hg determination" grade potassium dichromate in 800 mL of deionized water. Make up to 1 L using a volumetric flask.
1.8.3	3% Hydroxylamine hydrochloride/3% sodium chloride	Dissolve 30 g of "suitable for Hg determination" grade hydroxylamine hydrochloride and 30 g of sodium chloride in 800 mL of deionized water. Make up to 1 L using a volumetric flask. Filter solution through an 0.45 µm filter.

1.8.4 10% Hydrochloric acid — Carefully add, using a graduated cylinder, 100 mL of trace metal grade hydrochloric acid to 800 mL of deionized water. Make up to 1 L.

1.8.5 10% Stannous chloride — Transfer 100 g of stannous chloride to a 1 L beaker. Add 200 mL of H_2O and 50 mL of concentrated trace metal grade hydrochloric acid and heat on a hot plate until solution is clear. Make up to 1 L and filter.

1.9 Procedure

1.9.1 Clean all glassware with 1:1 nitric:sulfuric acid mixture.

1.9.2 Rinse with deionized water and oven dry.

1.9.3 Transfer a 20 mL aliquot of each sample and standard to a labelled graduated test tube.

(a) All samples should be done in triplicate. Prepare at least 3 blanks.

1.9.4 Add 1 mL of 4% potassium persulfate (1.8.1) to each tube.

1.9.5 Add 1 mL of 2% potassium dichromate (1.8.2) to each tube.

1.9.6 Slowly add 3 mL concentrated sulfuric acid to each tube and mix with a vortex mixer.

1.9.7 Place samples, standards and blanks in a steam bath for 30-45 minutes.

1.9.8 Allow samples to cool and cap tubes with Teflon lined caps until ready to analyze.

1.9.9 Set up continuous flow analyzer as shown in Figure 2.

1.9.10 Instrument settings:
lamp current: 6 ma
slit : 300 µm
wave length : 253.4 nm
heater : 30% at 120V

1.9.11 Transfer samples to auto-sampler cups and run.

(b) Include one standard after every nine samples (3 samples in triplicate).

1.10 Calculations

1.10.1 Measure peak heights of blanks, standards and samples.

1.10.2 Prepare calibration curve and read off sample concentrations.

1.10.3 Correct for any dilutions which were necessary.

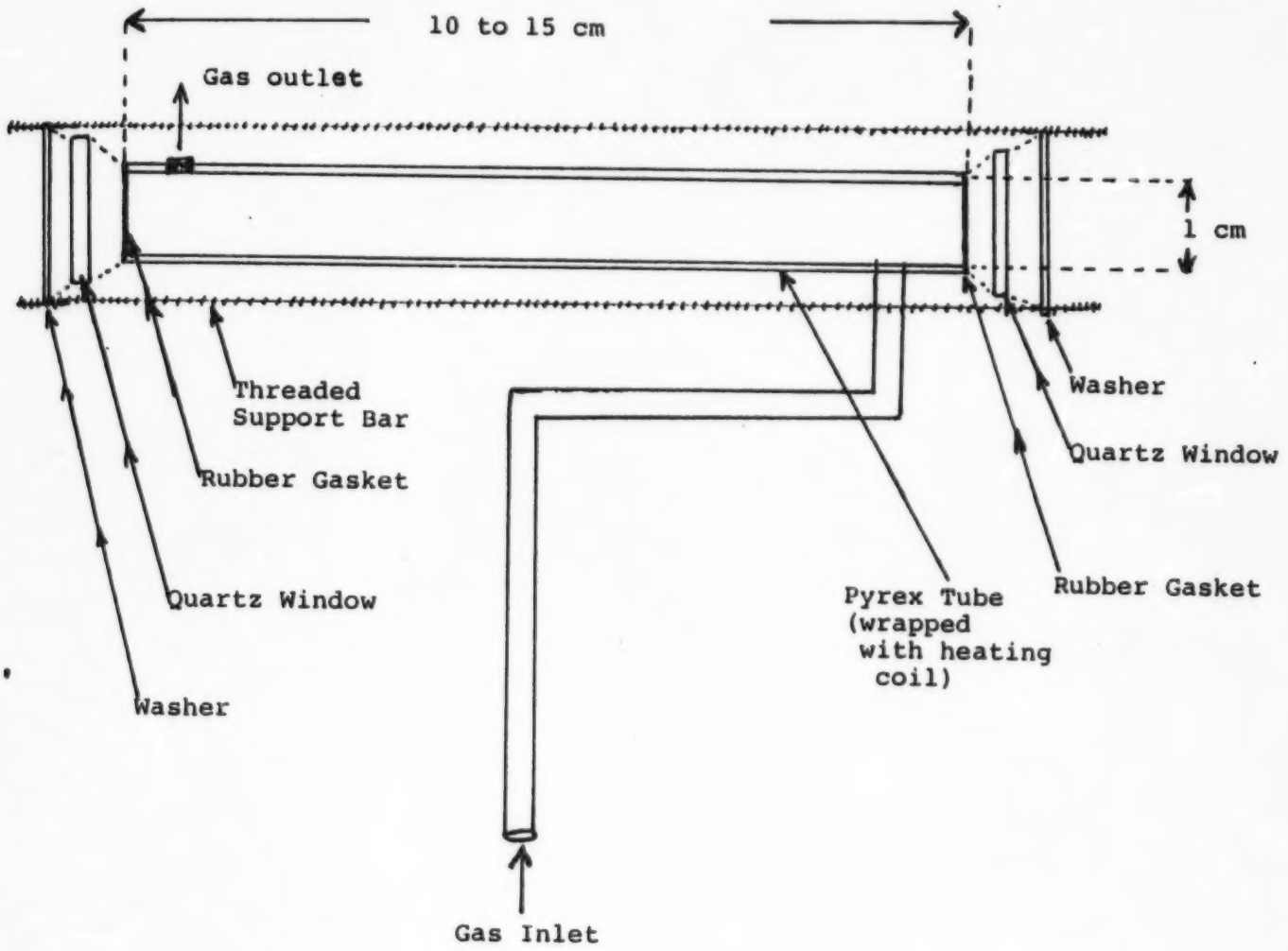

Figure 1
Mercury Cell

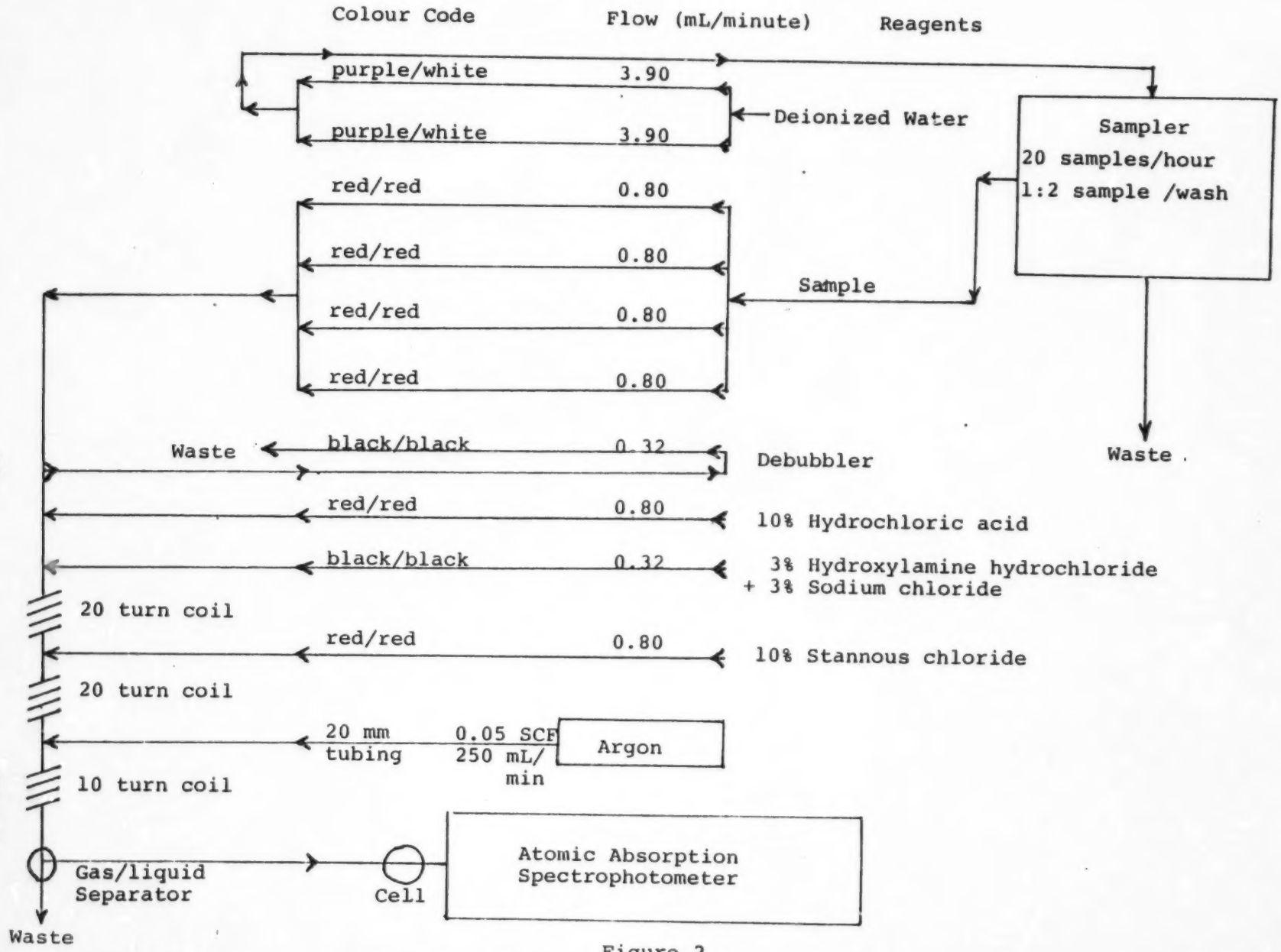

Figure 2
Mercury Cold Vapour Generation Flow Diagram

POOR

QUALITY

ORIGINAL